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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the nonaqueous electrolyte secondary battery provided with the anode containing a lithium content multiple oxide, the negative electrode which contains a dope and the carbon material which can be dedoped for a lithium ion, and the nonaqueous electrolyte made to come to dissolve a lithium salt electrolyte in a nonaqueous solvent. It is related with the nonaqueous electrolyte secondary battery excellent in high tension and the cycle characteristic on load discharging conditions in more detail.

[0002]

[Description of the Prior Art]In recent years, highly-efficient-izing of electronic equipment, a miniaturization, and portable-ization progress by progress of electronic art, and the demand of the high energy density battery used for these portable electronic devices has become strong. Although a nickel-cadmium battery, a lead battery, etc. are conventionally mentioned as a rechargeable battery used for these electronic equipment, By these cells, the actual condition has not fully met the demand of a cell with battery weight and a battery body product discharge potential (about 1.2V) is low, and large, and a high energy density.

[0003]These days, the nonaqueous electrolyte secondary battery which uses metal lithium and a lithium alloy as a negative electrode attracts attention as a battery system which fills these demands, and research is done briskly. However, in the case of the nonaqueous electrolyte secondary battery which uses metal lithium etc. as a negative electrode, there is a problem that neither a cycle life nor a rapid charge characteristic shows practically sufficient characteristic for the dissolution of metal lithium, the dendrite generation at the time of ****, or the minuteness making of deposit lithium.

[0004]Then, in order to solve these problems, research and development of the lithium ion nonaqueous electrolyte secondary battery which uses as a negative electrode the substance in which a dope and a dedope of a lithium ion are possible, for example, a carbon material, are activating. There is no problem about a fall of a cycle characteristic, a fall of a rapid charge characteristic, etc. to which the nonaqueous electrolyte secondary battery which uses such a negative electrode originates in a metal lithium negative electrode since lithium does not exist by a metallic state, and the outstanding battery characteristic is shown. Even if it compares with a nickel-cadmium battery, the low self-discharge nature needed as a rechargeable battery is also improved, and it has the advantage that moreover there is also no memory effect. Since the voltage (about 4.2V) of a cell becomes high by using a lithium content multiple oxide with a high oxidation-

reduction potential for an anode, it also has the advantage that the cell of high energy density is realizable. [0005]By the way, as nonaqueous electrolyte used for such a lithium ion nonaqueous electrolyte secondary battery, what dissolved electrolytes, such as LiPF₆, in nonaqueous solvents, such as cyclic carbonate or chain carbonic ester, is used. Especially, generally using the mixed solvent of propylene carbonate and diethyl carbonate is recommended as a nonaqueous solvent. By using such a mixed solvent as a nonaqueous solvent, even when a lithium ion nonaqueous electrolyte secondary battery is kept or used under high temperature service (for example, automatic in the car [of a summer], inside of the warehouse of heat-and-high-humidity atmosphere, etc.), degradation of a cycle characteristic can be controlled.

[0006]

[Problem(s) to be Solved by the Invention]However, when the mixed organic solvent of propylene carbonate and diethyl carbonate was used as a nonaqueous solvent of a nonaqueous electrolyte secondary battery, being unable to say that the cycle characteristic under high tension and load discharging conditions is enough, and also improving was called for.

[0007]The anode which this invention tends to solve SUBJECT of the above Prior art, and contains a lithium content multiple oxide, It aims at raising the high tension of the nonaqueous electrolyte secondary battery provided with the negative electrode which includes a dope and the carbon material which can be dedoped for a lithium ion, and the nonaqueous electrolyte which dissolves a lithium salt electrolyte in a nonaqueous solvent, and the cycle characteristic under load discharging conditions.

[0008]

[Means for Solving the Problem]By using oxalic acid diester as a nonaqueous solvent of an electrolysis solution, this invention person finds out that the above-mentioned purpose can be attained, and came to complete this invention.

[0009]Namely, a nonaqueous electrolyte secondary battery this invention is characterized by that comprises the following and with which a nonaqueous solvent is characterized by a thing of oxalic acid diester for which a kind is contained at least in a nonaqueous electrolyte secondary battery.

An anode containing a lithium content multiple oxide.

A negative electrode which includes a dope and a carbon material which can be dedoped for a lithium ion. Nonaqueous electrolyte which dissolves a lithium salt electrolyte in a nonaqueous solvent.

[0010]

[Embodiment of the Invention]As for the nonaqueous electrolyte secondary battery of this invention, a nonaqueous solvent is characterized by the thing of oxalic acid diester for which a kind is contained at least. Thereby, the high tension of a nonaqueous electrolyte secondary battery and the cycle characteristic under load discharging conditions can be raised.

[0011]The Reason such an effect is acquired is considered as follows, although it is not clear.

[0012]Namely, unlike usual fatty acid ester, since oxalic acid diester is ester of dibasic acid, Since reactivity with a metal ion is high compared with propylene carbonate, diethyl carbonate, etc. which are the conventional nonaqueous solvents, it is decomposed by the anode and this does not check an electrode reaction on a positive electrode surface, but it thinks for forming the stable coat which can bar disassembly of an impurity or a solvent molecule.

[0013]As oxalic acid diester used in this invention, a dimethyl oxalate, a diethyl oxalate, oxalic acid dipropyl,

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oxalic acid diisopropyl, an oxalic acid methylethyl, oxalic acid methylpropyl, oxalic acid ethylpropyl, etc. can be mentioned preferably. Especially, the point of an operational ease to a diethyl oxalate is preferred.

[0014]These oxalic acid diester can mix and use two or more sorts.

[0015]In this invention, although such oxalic acid diester may constitute 100% of nonaqueous solvents, it can be mixed and used [other / nonaqueous solvent and if needed], in that case -- since improvement in a cycle characteristic cannot be expected if there is too little content in the nonaqueous solvent of oxalic acid diester -- at least 1 capacity [of a nonaqueous solvent] % -- it is 5 capacity % preferably.

[0016]As a nonaqueous solvent which can be used together with oxalic acid diester, The nonaqueous solvent conventionally used in the lithium ion nonaqueous electrolyte secondary battery, For example, propylene carbonate, ethylene carbonate, butylene carbonate, gamma-butyrolactone, etc. which are high dielectric constant solvents, 1,2-dimethoxyethane, 2-methyltetrahydrofuran, dimethyl carbonate, methylethyl carbonate, diethyl carbonate which are low viscosity solvents, etc. can be mentioned.

[0017]The thing of the cyclic carbonate chosen from the group which consists of propylene carbonate, ethylene carbonate, and butylene carbonate especially for which a kind is used at least is preferred.

[0018]the case where a nonaqueous solvent is constituted from two-ingredient mixed stock of oxalic acid diester and cyclic carbonate -- the content in the nonaqueous solvent of oxalic acid diester -- desirable -- one to 95 capacity % -- it is 20 to 80 capacity % more preferably. On the other hand, the content in the nonaqueous solvent of the cyclic carbonate at this time is five to 99 capacity % preferably.

[0019]In this invention, it is preferred from a point of a cycle characteristic in addition to two ingredients of oxalic acid diester and cyclic carbonate, to add diethyl carbonate and to constitute a nonaqueous solvent from three-ingredient mixed stock.

[0020]the case where a nonaqueous solvent is constituted from three-ingredient mixed stock of oxalic acid diester, cyclic carbonate, and diethyl carbonate -- the content in the nonaqueous solvent of oxalic acid diester -- desirable -- one to 90 capacity % -- it is 20 to 80 capacity % more preferably. on the other hand -- the content in the nonaqueous solvent of the cyclic carbonate at this time -- desirable -- five to 50 capacity % -- it is ten to 40 capacity % more preferably -- the content in the nonaqueous solvent of diethyl carbonate -- desirable -- five to 50 capacity % -- it is ten to 45 capacity % more preferably.

[0021]As an electrolyte used when making it dissolve in the above nonaqueous solvents and preparing nonaqueous electrolyte, Generally, LiClO₄, LiAsF₆, LiPF₆, LiBF₄, LiCl and LiBr which are used as an object for lithium cells, CH₃SO₃Li, CF₃SO₃Li, etc. can be mentioned. Even if these are independent, they can mix and use two or more kinds.

[0022]As an anode of the lithium ion nonaqueous electrolyte secondary battery of this invention, what uses a lithium content multiple oxide is used as positive active material. Thereby, the rechargeable battery of a high energy density can be constituted.

[0023]as a lithium content multiple oxide, what is used can be conventionally used as positive active material of a rechargeable lithium-ion battery here -- especially -- formula (1)

[0024]

[Formula 2]Li_xMO₂ (1)

(among a formula, Co, nickel, and Mn are kinds at least preferably, and M is a transition metal and a number in which x satisfies 0.05<=x<=1.10.) -- the compound expressed can be used preferably. The value in [x] a

formula changes with charge-and-discharge states within the limits of $0.05 \leq x \leq 1.10$. Here, when the transition metal M is Mn, both $\text{Li}_x\text{Mn}_2\text{O}_4$ and Li_xMnO_2 can be used.

[0025]It faces forming an anode from such a lithium content multiple oxide, and a publicly known conducting material, a binding material, etc. can be added.

[0026]Such a lithium content multiple oxide can manufacture lithium and each salt of the transition metal M, for example, carbonate, a nitrate, sulfate, an oxide, hydroxide, a halogenide, etc. as a raw material, for example. For example, after measuring a lithium salt raw material and the charge of transition metal M Shiobara according to a desired presentation, respectively and fully mixing, it can manufacture by carrying out heating calcination under oxygen existence atmosphere in a temperature requirement (600 ** - 1000 **). In this case, the mixing method in particular of each ingredient is not limited, may mix powdered salts in the dry-type state as it is, or may dissolve powdered salts in water and may mix them in the state of solution.

[0027]As a negative electrode which constitutes a nonaqueous electrolyte secondary battery of this invention, although a carbon material in which a dope and a dedope are possible is used, a lithium ion, As such a carbon material, a low crystal carbon material produced by calcinating at a comparatively low temperature of 2000 ** or less, a high crystallinity carbon material which processed a raw material which is easy to crystallize at an about 3000 ** elevated temperature, etc. can be used. For example, pyrolytic carbon, corks, artificial graphites (pitch coke, needle coke, petroleum coke, etc.), natural graphite, glassy carbon, an organic polymer compound baking body (what calcinated and carbonized furan resin etc. at a suitable temperature), carbon fiber, activated carbon, etc. can be used. In a spacing of a field (002), 3.70 Å or more and true density Less than 1.70g/cc especially. And a low crystal carbon material which does not have an exothermic peak in not less than 700 ** by differential thermal analysis in an air air current, and high true specific gravity of negative electrode mixture restoration nature can use preferably a not less than 2.10g/cc high crystallinity carbon material.

[0028]It faces forming a negative electrode from such a material, and a publicly known binding material etc. can be added.

[0029]Suppose that it is the same as that of the conventional lithium ion nonaqueous electrolyte secondary battery about other composition, such as a separator of a nonaqueous electrolyte secondary battery of this invention, a battery can, a PTC element, and a charge collector. An assembly procedure of a cell can also be followed as usual.

[0030]It is not limited in particular for cell shape of a nonaqueous electrolyte secondary battery of this invention, but can be considered as various shape, such as cylindrical shape, square-shaped shape, a coin mold configuration, and a button mold configuration, if needed.

[0031]As explained above, since cycle characteristic of a nonaqueous electrolyte secondary battery of this invention under high tension and load discharging conditions is improving by using specific oxalic acid diester as a nonaqueous solvent, it becomes what was suitable as a power supply of various sized electronic equipment in recent years which needs load discharging.

[0032]

[Example]Hereafter, working example explains the nonaqueous electrolyte secondary battery of this invention concretely.

[0033]It explains concretely, referring to the sectional view of the cell shown in working example 1-21 and the comparative example 1 - 2 drawing 1.

[0034](Production of a negative electrode (1)) After introducing the functional group which contains oxygen in a petroleum pitch 10 to 20% (oxygen bridge construction), by calcinating at 1000 ** among inactive gas, Spacing =3.76 Å of the charge { (002) side of a difficulty graphitized carbon material of the character near a glassy carbon material (based on X diffraction measurement); true-specific-gravity =1.58} was obtained.

[0035]Next, the obtained carbon material was ground to powder with a mean particle diameter of 10 micrometers. Polyvinylidene fluoride 10 weight section was mixed as this powder 90 weight section and a binding material, negative electrode mixture was prepared, N-methyl-2-pyrrolidone was made to distribute this, and the negative electrode mixture slurry was prepared.

[0036]And this slurry was applied to both sides of copper foil of the 10-micrometer thickness which is a negative pole collector (10), and the band-like negative electrode (1) was produced by performing compression molding with an after-desiccation roll press machine.

[0037](Production of an anode (2)) First, lithium carbonate and cobalt carbonate were mixed so that it might become a ratio of 1.0 mol of 0.5-mol pairs, and LiCoO_2 was obtained by calcinating in the air at 900 ** for 5 hours.

[0038]Next, polyvinylidene fluoride 3 weight section was mixed with 2LiCoO_{91} weight section as a binding material with graphite 6 weight section as a conducting material as this positive active material, positive electrode mixture was prepared, N-methyl-2-pyrrolidone was made to distribute this, and the positive electrode mixture slurry was prepared.

[0039]Next, this slurry was uniformly applied to both sides of the aluminium foil of the 20-micrometer thickness which is a positive pole collector (11), and the band-like anode (2) was obtained by performing compression molding with an after-desiccation roll press machine.

[0040](Production of a nonaqueous electrolyte secondary battery) The band-like negative electrode (1) and anode (2) which were produced as mentioned above, By laminating in order the separator (3) which consists of a 25-micrometer-thick fine porosity polyethylene film, and winding a large number around the surroundings of a center pin, The swirl type electrode body of a size which is settled suitable for the iron battery cans (5) which performed the nickel plate, and (the outer diameter of 13.8 mm and 51.8 mm in height) was produced.

[0041]Next, in order to store this swirl type electrode body to a battery can (5), and to arrange an electric insulating plate (4) to those swirl type electrode body up-and-down both sides and to perform each current collection of an anode (2) and a negative electrode (1), It connected with the battery lid (7) via the safe valve gear (8) which drew the positive electrode lead (13) which consists of aluminum from the positive pole collector (11), and was provided with the PTC element (9) as a current cutoff device. The negative electrode lead (12) which consists of nickel was drawn from the negative pole collector (10), and it welded to the battery can (5).

[0042]Next, the nonaqueous electrolyte in which the mixed nonaqueous solvent shown in Table 1 - 3 was made to dissolve LiPF_6 by the concentration of 1 mol/l. was poured in into the battery can (5). And the battery lid (7) was fixed by closing a battery lid (7) and a battery can (5) via the gasket (6) which applied asphalt. This produced the 50-mm-high cylindrical nonaqueous electrolyte

secondary battery at 13.8 mm in diameter as shown in drawing 1.

[0043]

[Table 1]

(Capacity %) Working example nonaqueous solvent 1 2 3 4 5 6 7 8 dimethyl-oxalate 1 10 30 50 70 80 90 95 propylene-carbonate
99 90 70 50 30 20 10 5[0044]

[Table 2]

(Capacity %) Working example nonaqueous solvent 9 10 11. 12 13 14 15 diethyl-oxalate . 50 - - - - oxalic acid dipropyl . - 50 - -
--- oxalic acid diisopropyl . - - 50 - - - oxalic acid methylethyl . - - - 50 - - - oxalic acid methylpropyl - - - 50 - - oxalic acid
ethylpropyl - - - 50 50 propylene-carbonate 50 50 50 50 50 - ethylene carbonate - - - - 50[0045]

[Table 3]

(Capacity %) Working example comparative example nonaqueous solvent 16 17. 18 19 20 21 1 2 diethyl-oxalate 1 10 40 60 80 90
-- Propylene carbonate 45 45 30 20 10 5 50 - ethylene carbonate - - - - - 50 diethyl-carbonate 44 45 30 20 10 5 50 50[0046]

(Evaluation of battery capacity) The cycle-life examination shown below was done about the cylindrical nonaqueous electrolyte secondary battery of working example 1-21 and the comparative examples 1-2 which was carried out in this way and produced.

[0047] At the temperature of 23 **, it charges on the conditions of 2.5 h of charging time by the charge voltages 4.20V and 1000 mA of charging current, Then, the cycle which discharges on condition of the final voltage 2.75V by 250 mA of discharge current was repeated, the service capacity (Wh/l.) of 10 cycle eye and a 100 cycle eye was measured, and the ratio of the service capacity of the 100 cycle eye to the service capacity of 10 cycle eye was computed as capacitance retention (%). The obtained result is shown in Table 4.

[0048]

[Table 4]

	放電容量(Wh/l)	容量保持率
	100回目	100回目
実施例 1	2.20	81.8
2	2.40	85.4
3	2.60	90.4
4	2.40	89.6
5	2.60	90.4
6	2.65	90.6
7	2.30	87.0
8	2.10	85.7
9	2.40	89.6
10	2.65	90.4
11	2.60	86.5
12	2.65	86.8
13	2.60	84.5
14	2.50	84.0
15	2.50	84.0
16	2.50	90.0
17	2.60	88.5
18	2.65	88.7
19	2.65	90.6
20	2.50	92.0
21	2.20	81.8
比較例 1	2.30	78.5
2	2.45	75.5

[0049]The result of Table 4 shows that the capacity maintenance rate has been improved compared with the cell of the comparative examples 1-2 by which the mixed solvent of conventional cyclic carbonate and diethyl carbonate was used for the nonaqueous electrolyte secondary battery of working example 1-21 which uses oxalic acid diester as a nonaqueous solvent as a nonaqueous solvent.

[0050]When the mixed nonaqueous solvent of the two-component system of oxalic acid diester and propylene carbonate which are represented by the diethyl oxalate is used from the result of working example 1-7, it turns out that the desirable range of the content in the nonaqueous solvent of oxalic acid diester is in at least 1 - 95 capacity %. When the mixed nonaqueous solvent of three component systems of oxalic acid diester, propylene carbonate, and diethyl carbonate which are represented by the diethyl oxalate is used from the result of working example 16-21, It turns out that the desirable range of the content in the nonaqueous solvent of oxalic acid diester is in at least 1 - 90 capacity %.

[0051]

[Effect of the Invention]The anode which contains a lithium content multiple oxide according to this invention, and the negative electrode which includes a dope and the carbon material which can be dedoped for a lithium ion, The high tension of the nonaqueous electrolyte secondary battery provided with the nonaqueous electrolyte which dissolves a lithium salt electrolyte in a

nonaqueous solvent, and the cycle characteristic under load discharging conditions can be raised.

[Translation done.]